

Study on the fabrication processing of high-purity, high-density alumina green body prepared by a hydrothermal method

Hyeon Cheol Bae^a and Sang-Jin Lee^{a,b*}

^aDepartment of Advanced Materials Science and Engineering, Mokpo National University, Muan 534-729 Korea

^bThe Research Institute of Ceramic Industry Technology in Mokpo National University, Muan 534-729 Korea

Along with the recent increase in consumption of sapphire single crystals, the alumina green body of high-purity and high-density is required. The current manufacturing process for high-purity alumina using the aluminum or aluminum alkoxide compounds as a starting material had difficulties in mass production accompanied by the expensive equipments with high maintenance costs. Compared to this method, the high-purity alumina can be produced using the aluminum hydroxide dissolved in a caustic soda (sodium hydroxide) solution, in large quantity, with low cost. The mixing solution is aged for a certain period of time and then small amount of adsorbent is applied to selectively remove impurities in the solution. Finally a high purity alumina can be made from the refined solution. The alumina powders obtained through this method can be compacted and fired without any organic binder for the production of high-purity and high-density alumina green body. In this study, parameters in the manufacturing process employing the aluminum hydroxide to produce high-purity alumina were explored. And property changes of the final products were examined by varying the forming and firing parameters.

Key words: Sapphire single crystal, Alumina green body, Aluminum hydroxide, Hydrothermal method, Green density.

Introduction

In the Bayer process to produce alumina, the bauxite is dissolved into the caustic soda solution and then the aluminum hydroxides are precipitated through the re-crystallization process. In the aluminum hydroxide obtained from this Bayer process, the impurities originated from the bauxite and residuals of subsidiary raw materials added into the process are massively included. Thus the general manufacturing processes including the Bayer process have limitations in obtaining high-purity alumina. Techniques which have been used to produce high-purity alumina employed the re-crystallization process of aluminum hydroxide from the solution of high-purity aluminum dissolved with acids, or collected the alumina from high-purity aluminum compounds vaporized at high temperature. However, such methods are less productive in mass production, difficult to manipulate the processes, and expensive because of the use of high priced equipment and raw materials. And furthermore, there have been problems causing product damages in the manufacturing process and environmental pollutions [1-3]. To produce the sapphire ingot, the alumina green body is needed. In particular, to obtain the high quality sapphire ingot, the alumina green body should have good qualities such as high-density and high-purity without the presence of cracks [4, 5]. Since demands

for the sapphire having excellent optical or physical properties used for core components in precision technologies or in LED substrates have been increasing, the efficient and stable manufacturing process for sapphire is also needed [6]. Conventional methods to produce single crystal using alumina green body include the Verneuil method which grows the crystal at temperatures over 2,300 °C using H₂ and O₂, and the method employed the inductively coupled plasma to remove impurities from alumina at temperatures over 10,000 °C. However, such methods require highly expensive equipment and large energy consumption which caused them to be inefficient and less productive especially for the mass production due to small sized green compacts [7, 8].

In this study, the manufacturing conditions of high-purity alumina were examined with the high-purity aluminum hydroxide which was produced from general aluminum hydroxide dissolved in caustic soda solution by passing several processes through to eliminate fine impurities; and certain amount of AlF₃ was added as an alpha crystal accelerator. After controlling the primary particle size and morphology of the produced alumina powder, only a certain amount of ultrahigh-purity distilled water was added to obtain the green body to be fired later, that intended to create optimal processing conditions to produce the high-purity and high-density alumina green body [9, 10].

Experimental Procedure

Synthesis of high-purity aluminum hydroxide

*Corresponding author:
Tel : +82-61-450-2493
Fax: +82-61-450-2498
E-mail: lee@mokpo.ac.kr

The caustic soda solution of 210~280 g/L was prepared in an autoclave made of stainless steel (SUS 316L), and the general aluminum hydroxide containing moisture was added to be 0.62~0.74 wt% in the solution and stirred for 5 h under the pressure of 4 atm at 140 °C. Then the final solution was aged at different times under gradual decrease of temperature. In order to remove the impurities contained in the final solution different amount of pulps shaped filter were added so that the impurities could be adsorbed while the solution was stirred for 10 min at 5 rpm stirring speed under the fixed temperature of 100 °C at 2 atm pressure. The refined solution was then stirred with accelerated speed to precipitate the aluminum hydroxide by adding 40 g of aluminum hydroxide seeds (30 μm of average particle size) per 1 L of the solution together with varying the time and temperature of the precipitation process. Then the acquired precipitate was washed with distilled water at over 80 °C and then dissolved completely by adding sulfuric acid, and then re-crystallized by neutralization by applying 10% of ammonia water; after this it was washed again and filtered through to finally get the white, solid and high-purity aluminum hydroxide [11, 12].

Fabrication of high-purity, high-density alumina green body

The prepared high-purity aluminum hydroxide was completely dried and crushed, and then the 2.5 wt% of AlF_3 , based on the alumina amount calculated for the loss of ignition, was uniformly mixed with the powder and then fired at 1,050 °C for 1 h. After firing, the ultrahigh-purity distilled water was mixed with the alumina powder and then it was uni-axial pressed under 10 KN, and then fired at 1,750 °C for 2 h to get the high-purity, high-density alumina green body. The furnace used for the sintering was the box furnace with high-purity alumina refractory walls.

Characterization

The contents of caustic soda and alumina in the final solution were measured by titration method with the Titrando (Metrohm, 905 Dosing Unit System, Swiss). The analysis upon impurities was carried out using the ICP-OES (PerkinElmer, OPTIMA 7000DV, Germany) over the sample of 0.5~1.0 g which was dissolved by the pressurized acid hydrolysis method into the solution mixed with the high-purity sulfuric acid with ultrahigh-purity distilled water by ratio of 1 : 3 and then decomposed at 230 °C for 16 h. The mean particle sizes of the powder were analyzed using the Laser Particle Size Analyzer (Microtrac, S3500, USA), and the microstructures of the powder were observed through scanning electron microscopy (Hitachi, S-3500 N, Japan). Densities of the green body and fired sample were calculated by measuring the volume and weight of the disk shaped specimens. Here, the mean

values obtained from 5 measurements of each sample were used as the final data.

Results and Discussion

Contents of major impurities of the final solution in accordance with alumina/caustic soda weight ratio (A/C wt%) and NaOH concentration are presented in Fig. 1 and Fig. 2, respectively. When the A/C weight ratio of the final solution was varied with keeping the aging time constantly for 2 h, the impurities contents showed the minimum value at 0.72 of A/C weight ratio. The same minimal level of impurities contents were also observed at the 0.74 of A/C weight ratio (Fig. 1). At the condition over 0.74 of the A/C weight ratio, the reproducibility under given experimental conditions reduced quite seriously due to high degree of supersaturation that made it difficult to control the amount of impurities contents over the time required for the precipitation [13, 14]. When the concentration of

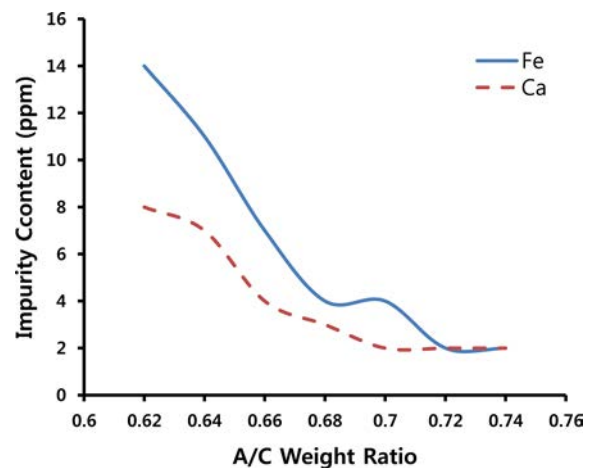


Fig. 1. Changes in contents of Fe and Ca impurities according to weight ratio of alumina and NaOH (A/C).

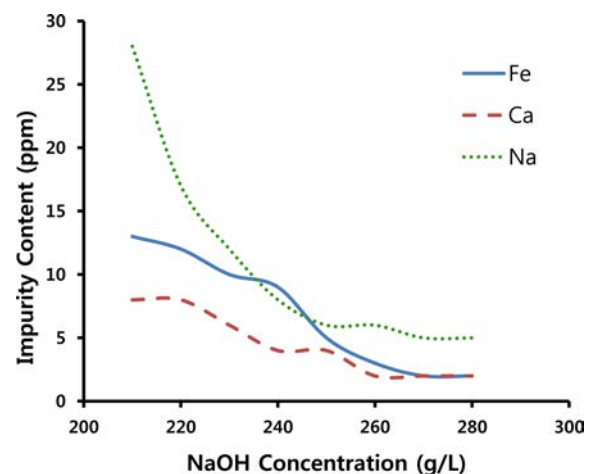


Fig. 2. Changes in contents of Fe, Ca, and Na impurities according to NaOH concentration at 0.72 of A/C weight ratio with aging time of 2 h.

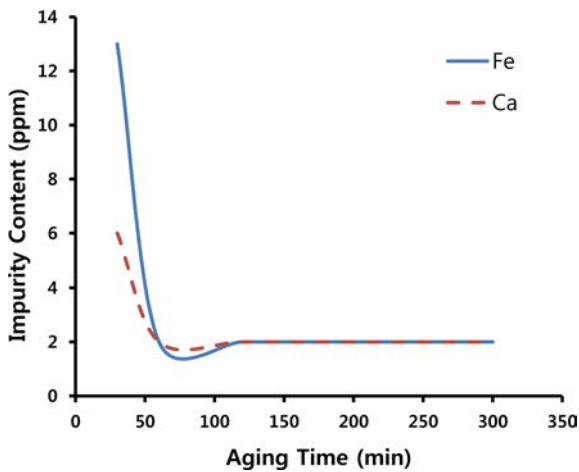


Fig. 3. Changes in contents of Fe and Ca impurities according to aging time at 0.72 of A/C weight ratio and 270 g/L of NaOH concentration.

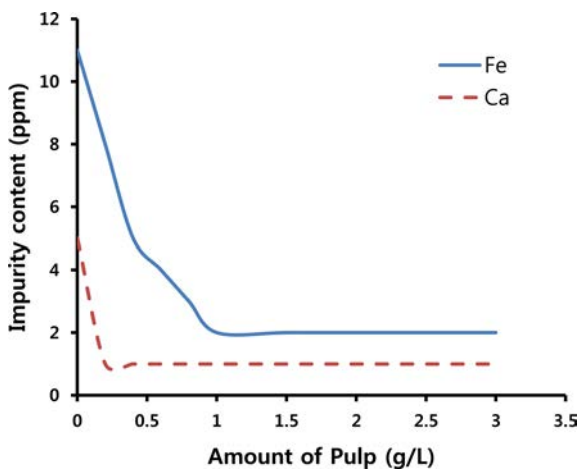


Fig. 4. Changes in contents of Fe and Ca impurities according to amount of pulp consumed (temp.: 100 °C, stirring speed: 5 rpm, stirring time: 10 min).

caustic soda was varied under aging times of constant 2 h at the 0.72 of A/C weight ratio, the lowest impurities contents were observed at the 270 g/L (Fig. 2). In the condition over 280 g/L of caustic soda amount, the rate of precipitation decreased due to increased viscosity of the final solution.

Changes in impurities contents along with the changes in aging time are illustrated in Fig. 3. When the aging time varied from 30 min to 300 min with the A/C weight ratio of 0.72 and the concentration of caustic soda of 270 g/L, the impurities contents reached the minimum level with the aging time of over 60 min. The level of impurities contents remained unchanged with further increase in the aging time. Fig. 4 shows the changes in impurities contents along with varying the amounts of pulp used from 0 to 3.0 g/L in the aged final solution. The temperature which could affect the level of impurities contents was kept constantly at 100 °C with a constant stirring speed of 5 rpm for 10 min. The removal efficiency of impurities was observed to be

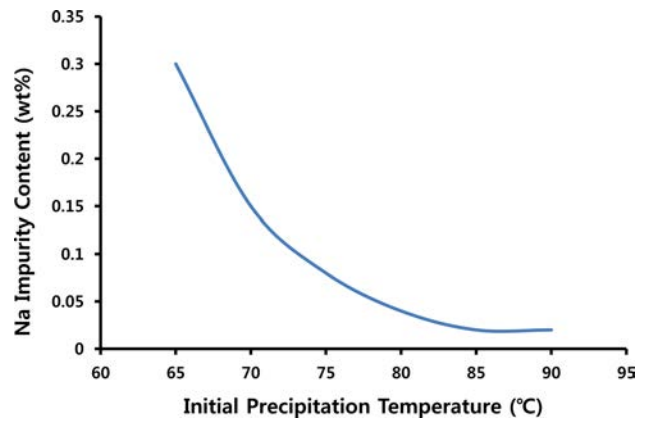


Fig. 5. Changes in content of Na impurity according to initial precipitation temperature after 72 h processing.

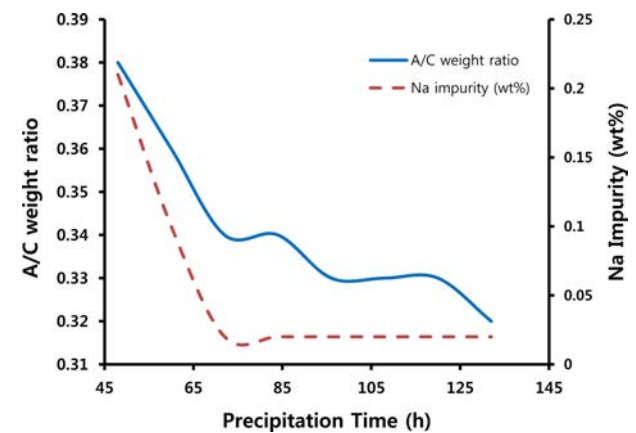


Fig. 6. Change in A/C ratio and Na impurity content according to precipitation time at initial precipitation temperature of 85 °C.

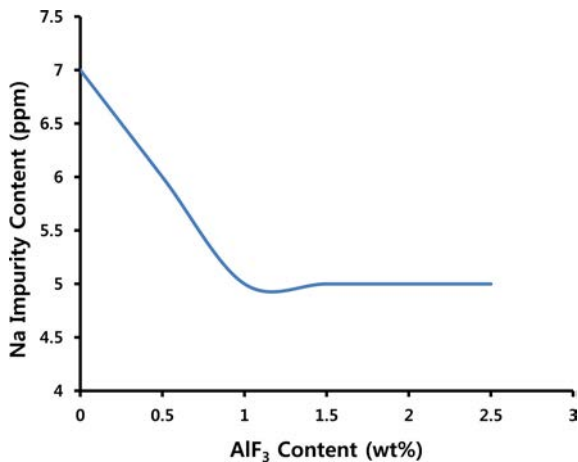
excellent when using over 1.0 g/L amount of pulp.

Based on the results of the experiments, the aluminum hydroxide seeds were put into the final solution and the changes in impurities contents along with changes in initial precipitation temperatures and times are presented in Fig. 5 and Fig. 6, respectively. The impurity content after 72 h precipitation processing showed the minimum level of impurity content of Na at the range of over 85 °C (Fig. 5). When the precipitation time varied from 48 h to 132 h at the temperature of 85 °C, the changes in A/C weight ratio and level of impurities contents were insignificant at the range over 72 h (Fig. 6). As a result, the precipitate of high-purity aluminum hydroxide having minimum impurities contents was obtained from the minimized content of caustic soda. The condition of precipitation at the minimized caustic soda was combined with 85 °C of initial temperature, 40 °C of final temperature, and 72 h of precipitation time which rendered the final A/C weight ratio below 0.34 wt%. Thus, the final A/C weight ratio below 0.34 was assumed to be the optimal processing condition allowing the quality and economy for the high-purity aluminum hydroxide.

Finally, the impurities contents in the high-purity aluminum hydroxide obtained through the final washing

Table 1. Impurities contents in high-purity aluminum hydroxide fabricated by hydrothermal method.

Impurity	Content (ppm)
Na	< 8
Fe	< 3
Si	< 2
Ti	< 2
Mg	< 1
Ca	< 1

**Fig. 7.** Changes in content of Na impurity according to applied amount of AlF₃.

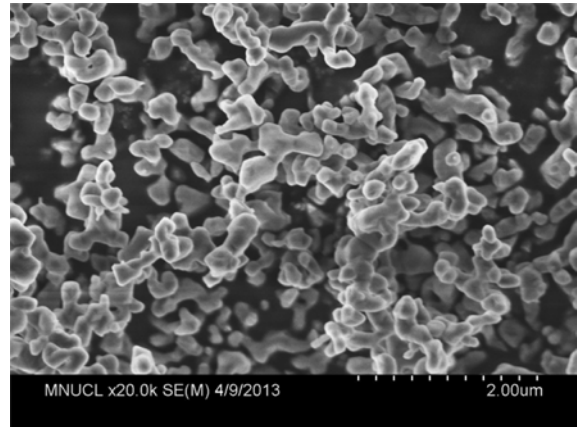
and recrystallization processes are summarized in Table 1. The very pure aluminum hydroxide of purity over 99.99% was obtained through the process and it is estimated that the level of impurity content can compete with foreign commercial high-purity aluminum hydroxide.

The obtained high-purity aluminum hydroxide was dried at 200 °C in the drying oven for 24 h to evaporate free waters and partially combined waters, and then crushed by roll milling. After mixing AlF₃ of 0 ~ 2.5 wt% based on alumina amount, the impurities contents of the fired powder were observed. The results are shown in Fig. 7. The Na impurity content showed constant values over the range of 1.0 wt% AlF₃. When the green body of high-purity aluminum hydroxide is to be made without any pre-treatment, it might be cracked or destroyed during firing process due to excessive inner vapor pressure caused by the vaporization of the combined water [15-17]. So the combined water should be completely vaporized to control the size and shape of primary particles for the forming of the green body and for this purpose, the AlF₃ was added.

The obtained alumina powder was classified by each particle size, and the green densities in accordance with the primary particle sizes of high-purity alumina and the densities of samples obtained after firing are summarized in Table 2. The green density revealed a value below 3.0 g/cm³ in the sample prepared from the alumina powder with the particle size over 3 μm. When the sample of density below 3.0 g/cm³ is used for the

Table 2. Changes in the density of high-purity alumina according to primary particle sizes.

Average particle size (D50, μm)	Green density (g/cm ³)	Fired sample density (g/cm ³)
0.1 ~ 0.5	1.8 ~ 2.3	3.5 ~ 3.7
0.5 ~ 2	1.6 ~ 2.2	3.3 ~ 3.5
2 ~ 3	1.5 ~ 1.8	3.0 ~ 3.5
3 ~ 10	1.2 ~ 1.5	2.5 ~ 3.0

**Fig. 8.** Microstructure of high-purity alumina powder prepared by hydrothermal method.**Table 3.** Changes in the Density of high-purity alumina according to D.I. water contents.

D.I. water content (wt%)	Green density (g/cm ³)	Fired sample density (g/cm ³)
0.01	0.9-1.2	3.0-3.3
0.5	1.5-2.3	3.2-3.6
1	1.6-2.3	3.5-3.8
2	1.8-2.4	3.5-3.9
5	1.9-2.4	3.5-3.9
10	1.9-2.4	3.5-3.9
15	1.9-2.4	3.5-3.9

manufacturing of sapphire ingot, the volume of alumina green body would increase and accordingly the productivity would also be decreased. Therefore, the primary particle size was controlled to be 0.1 ~ 0.5 μm to get the firing density of alumina green body over 3.5 g/cm³, and then the dense sample of which firing density ranged 3.5 ~ 3.7 g/cm³ were obtained. Fig. 8 shows the microstructure of primary particles of high-purity alumina powder with sizes of 0.1 ~ 0.5 μm. Although some agglomeration is observed, particle sizes are relatively uniform.

In the green body forming process with the high-purity alumina powder, ultrahigh-purity distilled water was applied instead of organic/inorganic binders to improve the cohesion force of particles for easy forming and to enhance the purity of green body. In this case, the applied pressure could be reduced, thus the impurities

Table 4. Impurities contents in high-purity alumina after forming and firing.

Impurity	Content (ppm)
Na	3
Fe	2
Si	2
Ti	1
Mg	0.5
Ca	0.5

**Fig. 9.** Photograph of fired high-purity, high-density alumina samples.

resulted from the abrasion of the mold surfaces could also be minimized. Changes in densities along with the amounts of ultrahigh-purity distilled water applied are listed in Table 3. The alumina powder of particle sizes ranging between 0.1 ~ 0.5 μm were used, and the best green densities were observed in the range of 2 ~ 15 wt%. When the 20 wt% of ultrahigh-purity distilled water was applied, moisture flow was observed during the pressing process. The impurities contents in the fired alumina samples are summarized in Table 4. Significant differences in comparison with the impurity content of high-purity aluminum hydroxide (Table 1) were not observed, however some contents of impurities were identified to be reduced slightly due to vaporization in the firing process. The final high-purity and high-density alumina samples completed the firing process show in Fig. 9.

Conclusions

In this study, the high-purity aluminum hydroxide was fabricated using the general aluminum hydroxide as the starting material through the hydrothermal methods of which processes consisted of dissolution, aging, filtration, adsorption, refining, reprecipitation

and acid/base reaction; and then the high-purity aluminum hydroxide was pressed and fired. The followings are the conclusions obtained from the experiments conducted in this study.

(1). The optimal economic process conditions of hydrothermal synthesis to produce high-purity aluminum hydroxide using general aluminum hydroxide were 270 g/L concentration of caustic soda, 0.72 of A/C weight ratio, 90 °C of initial precipitation temperature, 40 °C of final precipitation temperature, and 72 h of precipitation time which yielded the 99.99% of high-purity aluminum hydroxide.

(2). The primary particle sizes of the high-purity alumina powder to be pressed only with D.I. water should be controlled to have a range of 0.1 ~ 0.5 μm , and the optimal conditions of the fabrication process to make high-density alumina were 10 wt% of D.I. water application, 10 KN of forming pressure, 1,750 °C of firing temperature, and 2 h of firing time which allowed the creation of the high-density green body with its density over 3.7 g/cm³.

References

1. C. Misra, E.T. White, *J. Crystal Growth*, 8 (1971) 172-178.
2. D.J. Donaldson, *J. Metals*, 33 (1981) 37-41.
3. F. Habashi, *CIM Bulletin*, 81 (1988) 70-76.
4. H.S. Fang, Z.L. Jin, M.J. Zhang, Z. Zhang, and C.J. Zhao, *Int. J. Heat and Mass Transfer*, 67 (2013) 967-973.
5. I.D. Prendergast, D.W. Budworth, and N.H. Brett, *Trans. J. British Ceram. Soc.* 71 (1972) 31-36.
6. H.Y. Shin, J.H. Lim, and J.I. Lim, *J. Kor. Crystal Growth and Crystal Technology*, 23 (2013) 59-66.
7. Y.R. Um, M.G. Lee, and C.G. Lee, *J. Kor. Powder Metallurgy Institute*, 12 (2005) 422-427.
8. X.F. Fu, B.J. Xu, and C.J. Huang, *Adv. Mater. Res.* 734 (2013) 2496-2500.
9. Y. Yang, X. Jiao, B. Chen, and D. Chen, *J. Nanoparticle Res.* 15 (2013) 1-9.
10. N.K. Park, H.Y. Choi, D.H. Kim, T.J. Lee, M. Kang, W.G. Lee, H.D. Kim, and J.W. Park, *J. Crystal Growth*, 373 (2013) 88-91.
11. H.Y. Choi, D.H. Kim, and N.G. Park, *Clean Technology*, 18 (2012) 63-68.
12. G. Lu, Z. Wang, and D. Qiu, *Guang Pu*, 31 (2011) 244-248.
13. L. Qingsheng, Z. Chunming, and F. Hui, *Light Metals*, (2011) 197-200.
14. L.J. Liang, H. Jin, W.K. Jun, and Z.X. Qin, *China Int. Confer. High-Performance Ceram.* (2010) 805-807.
15. X.L. Wu, Q. Ren, and X.M. He, *Commun. Comput. Chem.* (2007) 2051-2053.
16. S.W. Kim and S.Y. Kim, *Solid State Phenomena*, 124 (2007) 831-834.
17. S. Zhang, S. Hu, and Z. Wei, *Chinese J. Rare Metals*, 28 (2004) 735-737.